

09.982.702
11.12.2003

LITERATUUR KOPIEEN

1021698

(12) **UK Patent Application** (19) **GB** (11) **2 289 672** (13) **A**

(43) Date of A Publication **29.11.1995**

(21) Application No **9510498.0**

(22) Date of Filing **24.05.1995**

(30) Priority Data

(31) **9410498**
9508222

(32) **25.05.1994**
22.04.1995

(33) **GB**

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(51) INT CL⁶

C02F 1/68 1/50 1/56 5/08

(52) UK CL (Edition N)

C1C CJB C200 C230 C253 C315 C40Y C400 C41Y C412
C483
U1S S1968

(56) Documents Cited

GB 2126579 A GB 1381673 A DE 002520360 A
US 4790943 A

(58) Field of Search

UK CL (Edition N) C1C
INT CL⁶ C02F

Online databases: EDOC, JAPIO, WPI

(54) Composition for treating cooling systems

(57) There is provided a composition for treating water cooling systems, the composition comprising a corrosion inhibitor such as polysilicate, a biocide such as stabilised chlorine dioxide and a flocculant, such as polyacrylamide.

The combination has surprising advantages and gives a general corrosion rate of less than 5 mpy with no pitting.

The use of a flocculant in the composition of the present invention enables the stripped biofilm to be completely removed and flushed from the system.

It is believed that this combination is a careful balance which overcomes the problems of scale, deposition, corrosion and microbiological fouling and would thus be effective against legionella whilst also being environmentally acceptable.

GB 2 289 672 A

1 **COMPOSITION FOR TREATING COOLING SYSTEMS**

2
3 The present invention relates to the cleaning and
4 sterilisation of industrial cooling towers, evaporative
5 condensers and associated pipework/equipment. It also
6 relates to the continuous treatment of such systems to
7 prevent corrosion, scaling, deposition and
8 microbiological contamination.

9
10 Water discharged from such systems in a controlled or
11 adventitious manner will enter factory or site drains.
12 It is important that the materials used are of low
13 toxicity or their discharge could adversely affect a
14 receiving stream.

15
16 Cooling water and its treatment still represents one of
17 the stiffest technical challenges in industry.
18 Arguably it is a problem which is still waiting for a
19 final solution. There have been solutions in the past
20 but these have been transient as further problems
21 associated with the cooling water system have been
22 identified or problems associated with the treatment
23 chemicals have been discovered.

24
25 There are four problems generally associated with
26 cooling water systems, namely corrosion, scaling,
27 deposition and microbiological fouling. All of these

1 problems are interrelated.

2

3 The water treatment industry has always recognised the
4 interrelationship between these issues but has never
5 set out to address the overall problem. The approach
6 has always been to attack a specific problem with a
7 specific chemical or group of chemicals and have one or
8 two other chemicals to either assist or to mop up the
9 consequences. At various times in the history of
10 cooling water treatment one of the four problems shown
11 above has assumed a greater importance and the industry
12 has geared itself up to finding products to deal with
13 that specific problem. In the 1960s and 1970s the
14 problems of scale and corrosion were identified as
15 being much more important than the other two. The lead
16 products were therefore corrosion inhibitors and scale
17 control chemicals and the effectiveness of a cooling
18 water treatment was measured in terms of how good a
19 corrosion rate and pitting index could be achieved with
20 minimal scaling. Good corrosion inhibitors could
21 therefore achieve corrosion rates of $< 5\text{ mpy}$ with no
22 pitting. These products were marketed fairly
23 aggressively by the water treatment companies with
24 claims that their use would minimise downtime, increase
25 thermal efficiency and give the plant operator peace of
26 mind.

27

28 It was recognised that cooling towers were air
29 scrubbers and that adventitious suspended solids could
30 get into cooling water. It was also recognised that a
31 cooling tower provides ideal conditions for
32 microbiological growth. Dispersants and biocides were
33 sold by the water treatment companies in support of the
34 corrosion/scale inhibitors but there were regarded as
35 secondary products.

36

1 Throughout the 1970s and the early 1980s scale and
2 corrosion inhibitors were the key products in the water
3 treatment market place and the only real change which
4 took place was the replacement of zinc chromate
5 formulations by more environmentally friendly products.
6 There are few people who would argue that zinc chromate
7 based formulations are the best cooling water
8 inhibitors from a price and performance viewpoint that
9 have ever been available. The factor which led to
10 their demise is that chromium is unacceptable in a
11 cooling water discharge to effluent. Many water
12 treatment companies did everything they could to
13 sustain the use of chromate based inhibitors, eg low
14 chrome blends and effluent treatment systems.

15
16 There are a number of lessons to be learned from this
17 phase of cooling water treatment.

- 18
19 1. The water treatment industry is driven by specific
20 problems.
- 21
22 2. Many of the chemicals used in cooling water
23 systems are relatively toxic and are eventually
24 replaced with more environmentally friendly
25 products.
- 26
27 3. The industry has struggled to replace the cost
28 efficient zinc chromate formulations.

29
30 The 1980s saw a change in the industry's approach to
31 cooling water treatment. Once again it was specific
32 problem driven, and it occurred almost from the moment
33 when cooling towers became linked with Legionnaire's
34 Disease and water was classed as a hazardous substance.
35 As a result the emphasis switched from scale and
36 corrosion control to that of deposition and

1 microbiological control. Biocides and their
2 effectiveness particularly against Legionella become
3 the selling focus for cooling water treatments. The
4 interest which surrounded the whole subject of
5 Legionella control in cooling water systems caused the
6 entire water treatment industry to re-examine its
7 approach.

8
9 However, while the emphasis moved and marketing changed
10 there was a dearth of innovative products. In many
11 instances it was simply a role reversal with biocides
12 and dispersants being promoted and scale and corrosion
13 inhibitors being moved back to their former position of
14 prominence. Dispersants and in particular
15 biodispersants became necessary to allow biocides to
16 penetrate slime deposits in cooling water systems. (In
17 general most conventional cooling water biocides will
18 kill bacteria with which they come into contact. They
19 will not penetrate biofilm).

20
21 All of the codes of practice spawned by Legionnaire's
22 Disease favoured seasonal disinfection of cooling
23 towers/systems. This basically means that on two
24 occasions per annum the system is thoroughly cleaned
25 and disinfected. Most of the procedures including
26 HS(G)70 for carrying out these seasonal disinfections
27 focus on the use of chlorine or chlorine based
28 materials. As it is well known that chlorine cannot
29 penetrate biofilm the use of biodispersants is also
30 advocated. There are a number of lessons to be learned
31 from this phase of cooling water treatment history.

32

33 1. During this period there was a little development
34 of biocide products but almost no development of
35 inhibitor/scale control formulations.

36

1 2. This phase recognised the presence of biofilm in
2 almost every water system. The water treatment
3 industry did not give biofilms the attention which
4 they merit and this is still very much the case.
5 HS(G)70 and other codes of practice do not help
6 this. They mention the existence of biofilm but
7 fail to address it seriously.

8
9 3. Many of the biocides which are used are fairly
10 toxic and could not be considered as
11 environmentally acceptable.

12
13 It may be concluded that the water treatment industry
14 has approached cooling water treatment by reacting to
15 whatever problem is current rather than trying to find
16 a more universal solution or approach. The possible
17 solutions are becoming more restricted by environmental
18 pressures and the range of chemicals which can be used
19 is diminishing. Many of the previous solutions, eg
20 chromate inhibitors, and chlorophenol and tin based
21 biocides could not be contemplated today and some of
22 the present solutions, eg zinc and molybdenum based
23 inhibitors and gluteraldehyde, sulphur based and
24 quaternary ammonium compounds are becoming unacceptable
25 due to environmental pressure. It is not inconceivable
26 that nitrites, phosphates and some of the milder
27 biocides will also come under environmental scrutiny in
28 the future.

29
30 The presence of biofilm has been acknowledged and while
31 some people in the industry have recognised its
32 importance water treatment companies have largely
33 ignored it.

34
35 The four major problems of cleaning water cooling
36 systems will now be discussed in detail below:

1. CORROSION

Cooling water systems can be complex comprising an assortment of metals in a variety of configurations subjected to a wide range of different conditions (temperature, flowrate, chemical concentration). It is very probable that almost every type of corrosion mechanism will be found in a very large cooling water system (eg in a refinery or petrochemical works) during the system lifetime. The types of corrosion found in a small system may be fewer but a cross section of small systems will exhibit a full range of corrosion problems. It is surprising that water treatment companies have so few people who fully understand cooling system corrosion or who could look at a specimen and be able to give a full account of the corrosion mechanism. It is also true to state that as the large operating companies become more lean and focus on their core activities that their level of in-house expertise will reduce. Many of these companies are already almost completely reliant on their water treatment contractor and as a consequence a lot of cooling system corrosion knowledge has been lost.

There are basically two classes of corrosion, namely general wastage where the whole metal surface is affected and localised corrosion which only a small area of the metal is affected. The first class is easier to deal with; the second is more clandestine and can appear in a variety of different guises.

The prevention of corrosion in cooling water systems has been approached fairly simplistically in the past in that inhibitors which either prevent the anodic reaction or the cathodic reaction from proceeding have been used. In a new system with perfectly clean rust-

1 free surfaces where the water conditions do not change
2 inhibition will be completely successful.
3 Unfortunately these conditions rarely, if ever, exist
4 and corrosion to some degree will occur in most
5 systems. Metal surface condition is fundamental to
6 corrosion protection and this is something which has
7 rarely been taken into account by the bulk of the water
8 treatment industry.

9
10 There are numerous accounts of disastrous attempts to
11 introduce a corrosion inhibitor into an old system
12 which is already exhibiting a fair degree of corrosion.
13 The water treatment industry has always relied on
14 laboratory evaluations to determine whether a cooling
15 water corrosion inhibitor performs well. The tests are
16 inevitably conducted on clean specimens under ideal
17 conditions where changes in the physical and chemical
18 conditions of the water are carefully controlled. In
19 almost every cooling water system there will be some
20 factor affecting the metal surface which will affect
21 the performance of the corrosion inhibitor. This may
22 be millscale which has been on the metal surface prior
23 to commissioning, surface irregularities arising from
24 weld spatter or poor fabrication, deposition of silt on
25 the metal surface or the formation of a biofilm on the
26 metal. The presence of deposits, differential
27 temperature, differential aeration, differential
28 concentration, crevice conditions will all thwart the
29 most efficient cooling water inhibitor. Similarly
30 water conditions can change markedly in a cooling
31 system because of temperature gradients, suspended
32 matter blowing in to the sump, adventitious leaks of
33 product and variable concentration factor.

34
35 Cooling water inhibitors can never be fully effective
36 and we have now appreciated that the main aim of any

1 cooling water treatment programme must be to give the
2 inhibitor the maximum chance of performing well, ie the
3 metal surface must be kept as clean as possible to
4 maximise the ability of the inhibitor to reach the
5 surface and protect the metal. If clean surfaces can
6 be achieved a relatively inefficient inhibitor can
7 offer better protection than a very efficient inhibitor
8 will give in a system where surface deposits and
9 biofouling obstruct the transport of the inhibitor to
10 the surface of the metal.

11

12 In UK Patent No. 1,379,074 Petrey managed to prove that
13 given deposit free surfaces a polysilicate-based
14 inhibitor could perform as well as a zinc chromate-
15 based formulation. In the 1960s Petrey tried to
16 persuade the marketplace that it was possible to have a
17 more environmentally friendly cooling water treatment
18 but his ideas were never adopted commercially. Thirty
19 years on, the environmental impact of cooling water
20 treatment chemicals is a serious issue and arguably if
21 a more environmentally acceptable treatment chemical is
22 available it should be used.

23

24 2. SCALE

25

26 Scale in cooling water systems consists almost entirely
27 of calcium carbonate and its presence can generally be
28 predicted from the chemical analysis of the circulating
29 water using Langelier and Ryznar Indices. Once again
30 any predictions based on these indices are general and
31 many unexpected scaling problems have occurred in
32 systems operating on soft water which have experienced
33 a small alkaline process leak in a critical exchanger.
34 The indices also do not take into account the roughness
35 or smoothness of the metal surface or the presence of
36 other surface foulants, all of which can be critical to

1 the initial formation and keying of the scale to the
2 metal surface.

3
4 Scale poses a number of problems in cooling water
5 systems. These are:

- 6
7 1. Loss of heat transfer. This is obvious and can be
8 critical from a process viewpoint as in general
9 the hotter the process the greater the tendency
10 for scale to form on the water side leading to
11 higher process temperatures etc. This cycle
12 ultimately leads to condenser blockage and process
13 shutdown on high temperature.
14
- 15 2. Resistance to flow. In the 1960s and 1970s a lot
16 of time and attention was given to the cost of
17 operating cooling water systems with and without
18 surface deposits and scale. Scale effectively
19 reduces the diameter of the pipework increasing
20 friction losses and pumping costs. 8% to 15% of
21 the power costs could be saved if metal surfaces
22 were kept clean.
23
- 24 3. Poor distribution. Scale can cause blockage and
25 partial blockages resulting in insufficient water
26 flowing to certain parts of the system. This will
27 tend to reduce the overall efficiency of the
28 system as there may be preferential cooling in
29 certain areas. Linked to this there can also be
30 scale deposits in the cooling tower itself which
31 can block channels leading to tower inefficiency.
32 Ultimately scale in the tower packing can lead to
33 packing collapse.
34
- 35 4. Treatment Absorption. One feature of scale is its
36 ability to absorb other treatment chemicals. This

1 can increase the cost of a particular treatment
2 and render certain biocide treatments ineffective.

3
4 5. Scale harbours micro-environments. Scale in
5 cooling water systems can be associated with
6 corrosion deposits, adventitious deposits and
7 biofilm. It can therefore be responsible for
8 protecting certain bacteria from biocide
9 treatment. It can also in certain situations lead
10 to under deposit corrosion.

11
12 From the discussion so far it can be seen that it is
13 not possible to control scaling in a cooling system by
14 controlling the Langelier or Ryznar Index. The most
15 cost efficient method of controlling scale is to use
16 threshold treatment chemicals. These are chemicals
17 which prevent the regular buildup of crystals and by
18 deforming the crystal lattice prevent the formation of
19 scale on a metal surface. The main advantage of
20 threshold chemicals is that they are not dosed
21 stoichiometrically and are therefore very cost
22 efficient. We believe that threshold chemicals backed
23 up with a chemical treatment which would keep the metal
24 surface clean would provide the ultimate scale control
25 programme. In general when a scale control programme
26 is being used a corrosion inhibitor will not be
27 required.

28
29 Once again we have now appreciated that control of
30 scale depends to a large extent on controlling surface
31 conditions and the key to successful scale and
32 corrosion control must be to keep the surface of the
33 metal clean.

34
35 3. DEPOSITION
36

The importance of keeping metal surfaces clean from corrosion products and scale has already been explained above. It is also clear that every attempt should be made to keep surfaces free from adventitious solids.

Suspended matter can get into the water in a cooling water system in a number of ways:

1. The cooling tower acts as an air scrubber in which any solids present in the air will be transferred into the aqueous phase.

2. Debris left behind during the construction phase can be picked up by the water flow and perhaps transferred to a more critical part of the system.

3. Process leaks can product solid material on the water side. This would be true in situations where there is an oil or hydrocarbon leak.

4. Airborne material can enter the tower sump.

5. Algae which can form in the upper well lit areas of some large cooling water towers can fall down under its own weight contributing suspended solids to the circulating water.

The composition of material found on the metal surface of any cooling system will be extremely variable. In addition to the rust/corrosion/scale deposits likely to be found there may also be a melange of silt/sand and an assortment of organic and inorganic debris. It is almost certain that there will be some microbiological activity associated with any such deposits.

There are a number of problems associated with

1 deposition. Severe deposition will ultimately lead to
2 blockage or poor distribution and as it is likely to
3 take place in low flow areas it is important that such
4 areas do not coincide with situations where design heat
5 transfer conditions are critical to the process.

6

7 In general most solids in the water end up in the tower
8 sump which effectively acts as a settlement tank.

9

10 Deposits on the metal surface can promote under deposit
11 attack by causing differential aeration conditions on
12 the metal surface.

13

14 It is this type of attack coupled with biofouling which
15 can create complex conditions on the metal surfaces in
16 cooling water systems. Deposits can provide the ideal
17 habitat for microbiological growth in that they can
18 often provide the food as well as the cover from
19 biocides.

20

21 Once again a situation is produced where the metal
22 surface and the complex interactions which take place
23 are critical to the integrity of the system from a
24 corrosion/scaling/deposition/microbiological viewpoint.
25 In our view if cooling water surfaces could be cleaned
26 and maintained in a clean condition most of the
27 problems associated with industrial water cooling
28 systems would disappear.

29

30 4. MICROBIOLOGICAL PROBLEMS

31

32 The understanding of the microbiology of a cooling
33 water system has increased dramatically over the past
34 twenty years. Arguably the most important discoveries
35 have still to be made. Planktonic-free swimming
36 bacteria rarely present any real problems to modern

1 biocide treatments and the concern today is what is
2 happening on the various surfaces in the system. The
3 development and maturing of biofilm on the surfaces of
4 a cooling water system holds the key to bacterial and
5 Legionella control in cooling systems.

6

7 The following statements are relevant:
8

9 1. Chlorine and bromine are not capable of
10 penetrating biofilm and systems which contain a
11 biofilm which has Legionella as part of the
12 sessile phase and are disinfected using these
13 biocides are capable of rapid reinfection.

14
15 2. Biofilms develop rapidly on surfaces which provide
16 a food source. This means that elastomers and
17 plastics will promote biofilm formation before
18 metals, particularly copper. Obviously metal with
19 a film of organic materials will promote biofilm
20 formation.

21
22 3. Modern understanding of biofilm shows that it
23 consists of a basal layer and a raised layer. The
24 basal layer is only 5 μ m thick whereas the raised
25 layer will extend into the water flow and interact
26 with materials dissolved or suspended in the water
27 flow.

28
29 4. One of the main problems associated with the
30 control of Legionella in water systems is
31 associated with its growth within an adherent
32 biofilm which comprises numerous other bacterial
33 species, protozoa and ciliates. Together these
34 form a complex balanced ecosystem in which the
35 Legionella are able to express several
36 physiological states; as planktonic cells, as free

1 living components of the biofilm ecosystem and in
2 association with amoebae, which may become
3 parasitised by the organism. It has been shown
4 that the presence of iron and other nutrients will
5 influence the type of Legionella. These factors
6 (in particular the host, the food source, and the
7 development of the biofilm) will all have an
8 influence on the efficiency of any biocide
9 treatment used to control Legionella.

10
11 It has now been appreciated that the activity at the
12 metal surface is vital to the success of any treatment
13 used for microbiological control in general and
14 Legionella in particular.

15
16 New biocides capable of penetrating biofilm and killing
17 amoeba are required.

18
19 The present invention considers all the problems faced
20 by existing cooling water treatments in the light of
21 some of the factors indicated in the foregoing
22 discussion.

23
24 The criteria for a cooling water treatment programme
25 according to the invention are:

- 26
- 27 1. The treatment must contain a constituent which
28 will help to keep metal surfaces clean.
 - 29
 - 30 2. The treatment must address the problem of biofilm
31 formation and development.
 - 32
 - 33 3. The materials used in the treatment must be as
34 environmentally friendly as possible.
 - 35
 - 36 4. The chemicals should be easy to dose and easy to

1 test.

2

3 5. The treatments should be compatible with existing
4 dosing systems and sterilisation techniques.

5

6 In the present invention a coagulant or polyelectrolyte
7 is used to remove debris from cooling system surfaces
8 by adding a biofilm penetrant and biocide, especially a
9 stabilised chlorine dioxide formulation to the
10 treatment package.

11

12 The philosophy behind the present invention is that if
13 clean surfaces can be maintained a less efficient but
14 also a much less toxic cooling water inhibitor is
15 sufficient, for example polysilicate solutions to
16 control corrosion when using polyelectrolytes and
17 chlorine dioxide.

18

19 In addition a threshold chemical to prevent scaling and
20 a maleic acid and phosphate copolymer may optionally be
21 used.

22

23 Drinking Water Inspectorate Approvals are available for
24 the inhibitor, biocide and polyelectrolyte/coagulants
25 used.

26

27 The present invention provides a composition for
28 treating water systems, said composition comprising a
29 corrosion inhibitor, a biocide and a flocculent.

30

31 Generally, the biocide may be any chlorine dioxide
32 based biocide. One particularly convenient biocide is
33 stabilised chlorine dioxide, which is a buffered
34 solution of chlorine dioxide gas in an aqueous system.
35 Normally simple salts, such as sodium carbonate, are
36 included to provide the buffering effect. The

1 solubility of chlorine dioxide in aqueous media is low
2 and generally solutions higher than 5% (weight:volume)
3 cannot normally be achieved. Any concentration of
4 stabilised chlorine dioxide may be used in the present
5 invention, but particular mention may be made of 2%-5%
6 (weight:volume) concentration in the composition. The
7 pH of the stabilised chlorine dioxide solution may be
8 adjusted as required. For example a pH of from 7 to
9 10, especially 7-7.5 up to 9-9.5 may be suitable.
10 Commercially available stabilised chlorine dioxide
11 solutions are available, such as BIOX™ from Viscona and
12 PURAGENE™ from Vernacare. Optionally 20-30 ppm,
13 especially approximately 25 ppm of chlorine dioxide
14 should be generated during sterilisation procedures.

15
16 ~~Any chlorine dioxide may be neutralised, for example~~
17 ~~with sodium thiosulphate, prior to drainage.~~

18
19 An advantage of using a chlorine dioxide based biocide
20 is its ability to strip biofilm, the deposit of
21 bacteria which adheres to the internal surface of pipes
22 etc.

23
24 Generally, the corrosion inhibitor may be a
25 polysilicate, especially a polysilicate salt such as
26 sodium polysilicate. Suitable quantities of
27 polysilicate or polysilicate salt in the composition
28 include an aqueous solution of up to 30%
29 (weight:volume). However concentrations of less than
30 this, for example about 8 to 15% by weight:volume may
31 be suitable for certain systems.

32
33 Other additives, including hydroxyethylene
34 diphosphonate (HEDP), methylenebenzyltriazole (MBT)
35 and/or polyacrylates (from a commercial source) may
36 also be present, if required. Advantageously a

1 polysilicate corrosion inhibitor may be used in
2 combination with a polyacrylate. Generally the
3 silicate level in the treated water system will be in
4 the region of from 20 ppm to 100 ppm, preferably 40 ppm
5 to 60 ppm.

6
7 However, any material which acts to keep the biocide in
8 a dispersed form may be acceptable.

9
10 The flocculant may be a polyelectrolyte (alternatively
11 termed a "mud mover"). Such additives are known in the
12 art and are used to flocculate solid material, thus
13 keeping metal surfaces clean. Examples of suitable
14 polyelectrolytes include polyacrylamides. Depending
15 upon the system if the polyacrylamides chosen may be
16 anionic, non-ionic or cationic. Especially suitable
17 anionic polyacrylamides include those of low charge and
18 with a molecular weight of 5-50kDa, especially 15-
19 25kDa.

20
21 Suitable non-ionic polyacrylamides may be of a
22 molecular weight of 5-50kDa, especially 15-25kDa.
23 Suitable cationic polyacrylates include those of high
24 charge and with a high molecular weight, for example
25 over 50kDa.

26
27 The combination of polysilicates and polyelectrolytes
28 has surprising advantages and gives a general corrosion
29 rate of less than 5 mpy with no pitting.

30
31 The use of a flocculant in the composition of the
32 present invention enables the stripped biofilm to be
33 completely removed and flushed from the system.

34
35 The present invention further provides the use of a
36 composition containing a corrosion inhibitor a biocide

1 and a flocculant for cleaning, and preferably
2 sterilising, a water system.

3
4 Further, the present invention provides a method of
5 cleaning (and disinfecting) a water system, said method
6 comprising the addition of a corrosion inhibitor, a
7 biocide and a flocculant to said system. It is not
8 necessary that all the active ingredients are added
9 together, although in certain applications that may be
10 desirable. Thus in some situations it may be
11 acceptable to add the ingredients sequentially.

12
13 In a further aspect, the present invention provides a
14 kit for cleaning water systems, said kit comprising:

- 15
16 a) a corrosion inhibitor;
17 b) a biocide; and
18 c) a flocculant

19
20 wherein optionally at least one of the components
21 listed above is packaged separately.

22
23 In a further aspect, the present invention provides the
24 use of a corrosion inhibitor in the manufacture of a
25 composition according to the present invention.

26
27 In a further aspect, the present invention provides the
28 use of a biocide in the manufacture of a composition
29 according to the present invention.

30
31 In a further aspect, the present invention provides the
32 use of a flocculant in the manufacture of a composition
33 according to the present invention.

34
35 We do not consider that the techniques and chemicals
36 which are used at present and are advocated by the

1 Health and Safety Executive can guarantee the
2 elimination of Legionella risk from cooling water
3 systems. Work has indicated that the biocides
4 currently used, and particularly the halogens, will not
5 penetrate biofilm or destroy the amoeba which can act
6 as host for the Legionella bacterium. CAMR have for
7 instance reported that a bromine level of 8 mg/l had no
8 effect on Legionella hidden in a surface biofilm and
9 work at Sheffield (Hallam) University has indicated the
10 failure of chlorine to kill host Amoeba when used at
11 levels recommended by HS(G)70.

12
13 It is also the experience of the water treatment
14 companies and cooling tower operators that following
15 the recommendations of HS(G)70 does not necessarily
16 prevent proliferation of Legionella bacteria. The
17 complexity of cooling water systems, the variety of
18 different materials and the possibility of amoeba and
19 biofilm hideout means that current thoughts on
20 acceptable biocides may not be valid.

21
22 We believe that chlorine dioxide is a fundamental
23 ingredient of any water treatment which claims to be
24 effective against Legionella. There is already a body
25 of practical information available to suggest that
26 chlorine dioxide can penetrate and remove biofilm. On
27 many occasions large quantities of biofilm have been
28 removed from systems which had been recently
29 disinfected with chlorine. This will be the claim of
30 many operators who routinely use chlorine dioxide for
31 sterilisations or for those who have been asked to
32 perform a sterilisation on a cooling tower which has
33 been routinely disinfected using hypochlorite solution
34 and is disinfected for the first time using chlorine
35 dioxide. It is one of the underlying claims of the
36 Liverpool Broadgreen Hospital report where chlorine

dioxide replaced bleach as the biocide and removed the Legionella risk from the hospital hot water systems which had been the cause of recurring Legionella problems while operating on a chlorine based regime.

Chlorine dioxide has found little application as a cooling water treatment biocide in the past and there have been good reasons for this.

1. Almost all of the chlorine dioxide used for water treatment was produced using generators. Generators got themselves a bad reputation in the past as some of the early ones were poorly made and managed to blow themselves apart. Chlorine dioxide generators represent a fair capital investment which would not be considered appropriate for many small and medium sized cooling water systems.
2. Chlorine dioxide cannot be transported and must be produced on site. This involves the handling of chemicals which would be considered as hazardous.
3. While much is known about chlorine dioxide as a disinfectant in the potable water treatment industry little is known about it as a cooling water biocide. There are in fact few bacterial and viral strains against which chlorine dioxide is not completely effective.
4. The advent of stabilised chlorine dioxide to this country is relatively recent and all the major water treatment companies have decided not to add it to their product portfolio at present. This is a decision which they will almost certainly revoke as information on the effectiveness of these

1 products becomes more widespread.

2
3 5. Stabilised chlorine dioxide has been compared
4 unfairly with bleach (14.5% free chlorine) as a
5 disinfectant in situations where it is used as a
6 direct replacement. If it is assumed that bleach
7 can be sold for around £0.35/litre and chlorine
8 dioxide is 7 times more efficient than chlorine
9 then a 2% chlorine dioxide solution should be
10 roughly the same price, ie £0.35/litre. In fact
11 the price will be roughly 10 times this and one of
12 the greatest hurdles which stabilised chlorine
13 dioxide will have to leap is this invidious price
14 comparison with bleach. The material cost
15 competes well with the other commonly used
16 biocides.

17
18 It is clear from the more recent outbreaks of
19 Legionnaire's Disease that a new product needs to be
20 used as the standard disinfectant in water systems, and
21 in particular the more complex cooling water systems.
22 We believe that this need is fulfilled by the
23 composition of the present invention.

24
25 The value of a thorough clean and disinfection using
26 chlorine dioxide should not be understated. If a
27 system can be brought to a condition of "industrial
28 sterility" then ongoing treatment becomes
29 straightforward and relatively non problematic.

30
31 People require to change their thinking about the
32 importance of the seasonal disinfection. It is not
33 something that is done twice per annum as a
34 microbiological purging of the system. It is something
35 that is done to give the Delta PA treatment a firm
36 foundation. Often after this first disinfection

1 microbiological control can be effected by dosing the
2 stabilised chlorine dioxide based product without
3 activation.

4
5 When the biofilm has been completely removed and it is
6 only adventitious bacteria entering the system which
7 need to be dealt with then the stabilised material can
8 activate itself on the acidic cell wall of the
9 bacterium releasing the chlorine dioxide will kill the
10 bug.

11
12 This sort of situation required careful monitoring and
13 any sudden increases in microbiological population
14 needs to be addressed by activating the product. The
15 level of activation will depend on the type of system
16 and the particular problem.

17
18 Some systems only need a shock dose perhaps once or
19 twice per week to control the bug count; others may
20 require a variation between of stabilised and activated
21 chlorine dioxide.

22
23 A further constraint on dosing is that the DELTA PA
24 Programme is being marketed as being environmental
25 friendly and the ongoing treatment level should if
26 possible be confined to 1 mg/l to 3 mg/l.

27
28 It is for this reason that the effectiveness of the
29 disinfection is stressed. When it is conducted
30 properly and the neutralisation of residual chlorine
31 dioxide has been completed then the system should be
32 controlled by low level dosing of the DELTA PA 6 range.
33 Any sudden increase in the chlorine dioxide demand must
34 be treated as an emergency situation requiring a mini
35 on-line disinfection with neutralisation of any
36 blowdown from the system.

EXAMPLE

While each cooling water system treatment regime is customised the treatment proposed uses three chemicals:

1. DELTA PA 4 Series which are inhibitors based on sodium polysilicate

2. DELTA PA 6 Series of biocides which are based on "BIOX" a stabilised chlorine dioxide product.

3. DELTA PA 8 Series of flocculant materials.

The inhibitor and the flocculant are dosed in proportion to the make up water to the system. The concentration in the make up will depend on the concentration factor in the system but we would normally expect a silicate level of 20ppm to 30ppm. The flocculant is dosed at a level of 10ppm to 100ppm depending on the product used.

The biocide can be dosed in a variety of ways eg continuously, on a batch basis, or depending on circumstances both. The biocide be dosed in the activated or non-activated form but generally at a maximum level of 1 or 2ppm in the cooling water. At the use level none of the materials used can have an adverse effect on the stream which receives the blowdown water from the cooling water system.

Experimental work has shown:

1. The DELTA PA system achieves corrosion rates of <3 mpy and no pitting on mild steel. Corrosion rates on copper, copper alloys and stainless steel are

1 <1 mpy.

2

3 2. Metal surfaces are kept free from biofilm and
4 surface debris. This improved heat transfer and
5 therefore energy efficiency improves the overall
6 performance of the cooling water system.

7

8 3. All of the chemicals used are used in the
9 treatment of potable water, are all approved by
10 the Drinking Water Inspectorate and therefore are
11 of low toxicity. This has been confirmed by
12 Microtox testing.

13

14 4. The treatment is more effective if started
15 immediately after a clean and sterilisation of the
16 cooling tower using chlorine dioxide and polymer.
17 The DELTA PA 6 product is activated and dosed at a
18 rate to give 20 ppm ClO_2 in the cooling water.

19

20 The DELTA PA 8 product is dosed to ensure that
21 biofilm and debris removed by the clean are
22 dispersed and flocculated suitable for removal
23 from the system. The unused chlorine dioxide in
24 the waste water from the clean is treated with
25 sodium thiosulphate or hydrogen peroxide prior to
26 discharge.

27

28 5. The DELTA PA system lends itself to chemical
29 cleaning of critical heat exchangers fouled with
30 biofilm and iron oxide by adding inhibited citric
31 acid with the DELTA PA 6 and DELTA PA 8 product.
32 These cleans can be conducted on or off line
33 depending on circumstances.

34

35 The chemicals which comprise the range to date are
36 therefore:

1 1 DELTA PA 400 Series inhibitors and scale control
2 chemicals.

3
4 DELTA PA 441 polysilicate concentrate 29% SiO_2 dosed to
5 give 10 to 30 ppm product in the system. This product
6 is used for large systems.

7
8 DELTA PA 442 is a 1:1 dilution of this product and

9 DELTA PA4410 is a 10:1 dilution of this product.

10
11 DELTA PA 450 polysilicate and multichemical formulation
12 dosed to give 70 ppm to 100 ppm in the system. This
13 chemical is used in multimetal systems where something
14 more efficient than a basic polysilicate is preferred.
15 It is less environmentally friendly than DELTA PA 441.
16 This formulation is also available as a 5:1 dilution
17 called DELTA PA 445.

18
19 DELTA PA 470 polymer and phosphonate for threshold
20 effect scale inhibition. This is dosed at 25 ppm to 40
21 ppm. Available as DELTA PA 471 which is a 1:1 dilution
22 of DELTA PA 4710 as a 10:1 dilution.

23
24 DELTA PA 6 Series biocides.

25
26 The biocides are based on stabilised chlorine dioxide
27 and comprise DELTA PA 62 a (2% stabilised chlorine
28 dioxide solution) and DELTA PA 65 (a 5% stabilised
29 chlorine dioxide solution).

30
31 The formulations may contain biodegradable surfactants
32 and are less highly buffered than the conventional
33 products. The real value of these products is in the
34 range of activation techniques which could be used.

35
36 DELTA PA 8 Series: Coagulants and polymers.

1 A full range of cationic organic coagulants based on
2 organic materials (non aluminium) are included in the
3 programme..

4

5 A full range of polyelectrolytes is included in the
6 range although there is a core of three products
7 representing cationic, non ionic and anionic products.

8

9 Anionic polymers are best suited to inorganic and inert
10 debris, eg silt and sand, while a strong cationic
11 polyelectrolyte is best suited to oily deposits and
12 organic debris.

13

14 We believe that the incorporation of chlorine dioxide
15 into the microbiological control package is fundamental
16 to Legionella control because the PA 6 series of
17 biocides offers something that other commonly used
18 biocides do not.

19

CLAIMS

1. A composition for treating water systems, said composition comprising a corrosion inhibitor, a biocide and a flocculant.
2. A composition as claimed in Claim 1 wherein said biocide is based on chlorine dioxide.
3. A composition as claimed in Claim 2 wherein said biocide is a buffered solution of chlorine dioxide gas in an aqueous system.
4. A composition as claimed in either one of Claims 2 and 3 wherein the concentration of chlorine dioxide is 2% to 5% (weight : volume).
5. A composition as claimed in any one of Claims 1 to 4 wherein said corrosion inhibitor is a polysilicate.
6. A composition as claimed in Claim 5 where the concentration of polysilicate is up to 30% (weight : volume).
7. A composition as claimed in any one of Claims 1 to 6 wherein said flocculant is a polyacrylamide.
8. A composition as claimed in any one of Claims 1 to 7 which further comprises hydroxydiphosphonate (HEDP), methylenebenzyltriazole (MBT) and/or polyacrylates.
9. Use of a composition as claimed in any one of Claims 1 to 8 for cleaning a water system.

- 1 10. A method of cleaning a water system, said method
2 comprising the addition of a corrosion inhibitor,
3 a biocide and a flocculant to said system.
4
- 5 11. A kit for cleaning water systems, said kit
6 comprising:
7
8 a) a corrosion inhibitor;
9 b) a biocide; and
10 c) a flocculant
11
12 wherein optionally at least one of the components
13 listed above is packaged separately.
14
- 15 12. A composition for treating water systems
16 substantially as defined in the Example.



Application No: GB 9510498.0
Claims searched: 1-12

Examiner: Diane Davies
Date of search: 9 August 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): C1C

Int Cl (Ed.6): C02F

Other: Online databases: EDOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2126579 A (Buckman Labs Inc.) Ammonium salts which act as flocculants, microbicides and corrosion inhibitors.	1
X	US 4790943 A (SE Water Conservation Systems Inc) Treatment of waste water with biocide and flocculants	1-12
X	DE 2520360 A (Wabag Wasserreinig) Use of oxidant and flocculant to purify and sterilise water from swimming pools.	1-12
X	GB 1381673 A (J. O'Shea <i>et al</i>) A method of chemical treatment of water supplies, see in particular the list of chemicals on page 3.	1-12

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.